PB83-119198

Revised Test Methods 106 and 107
(Proposed November 18, 1980, 45 FR 76346)
Summary of Comments and Responses

(U.S.) Environmental Protection Agency
Research Triangle Park, NC

Jan 82

U.S. Department of Commerce
National Technical Information Service
NTIS

TECHNICAL REPORT DATA
(Please read Instructions on the reverse before completing)

1. REPORT NO.	2.	3. RECIPIENT'S ACCESSION NO.
EPA 450/3-82-002		PB83 119198

4. TITLE AND SUBTITLE	5. REPORT DATE
Revised Test Methods 106 and 107 - (Proposed November 18, 1980, 45 FR 76346) Summary of Comments and Responses	January 1982
	6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S)	8. PERFORMING ORGANIZATION REPORT NO.
Emission Standards and Engineering Division	
9. PERFORMING ORGANIZATION NAME AND ADDRESS	10. PROGRAM ELEMENT NO.
Emission Measurement Branch (MD-19) Emission Standards and Engineering Division U. S. Environmental Protection Agency Research Triangle Park, N. C. 27711	11. CONTRACT/GRANT NO.
12. SPONSORING AGENCY NAME AND ADDRESS	13. TYPE OF REPORT AND PERIOD COVERED
DAA for Air Quality Planning and Standards (MD-10) Office of Air, Noise, and Radiation U. S. Environmental Protection Agency Research Triangle Park, N. C. 27711	14. SPONSORING AGENCY CODE EPA/200/04

15. SUPPLEMENTARY NOTES

16. ABSTRACT

This document addresses the public comments submitted after proposal of the vinyl chloride methods in the Federal Register. Changes made to the methods as a result of these comments are included. This document serves as the basis for the revisions which have been made to the test methods between proposal and promulgation.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
		13 B

18. DISTRIBUTION STATEMENT	19. SECURITY CLASS (This Report)	21. NO. OF PAGES
Release Unlimited	Unclassified	23
	20. SECURITY CLASS (This page)	22. PRICE
	Unclassified	

United States
Environmental Protection
Agency

Office of Air Quality
Planning and Standards
Research Triangle Park NC 27711

EPA-450/3-82-002
January 1982

Air

PB83-119198

EPA

Revised Test Methods 106 and 107- Summary of Comments and Responses

REPRODUCED BY
NATIONAL TECHNICAL
INFORMATION SERVICE
U.S. DEPARTMENT OF COMMERCE
SPRINGFIELD, VA. 22161

ESED

EPA-450/3-82-002

Revised Test Methods 106 And 107-
(Proposed November 18, 1980, 45 FR 76346)

Summary Of Comments And Responses

Emission Standards and Engineering Division

U.S. ENVIRONMENTAL PROTECTION AGENCY
Office of Air, Noise, and Radiation
Office of Air Quality Planning and Standards
Research Triangle Park, North Carolina 27711

January 1982

This report has been reviewed by the Emission Standards and Engineering Division of the Office of Air Quality Planning and Standards, EPA, and approved for publication. Mention of trade names or commercial products is not intended to constitute endorsement or recommendation for use. Copies of this report are available through the Library Services Office (MD-35), U. S. Environmental Protection Agency, Research Triangle Park, N. C. 27711, or from National Technical Information Services, 5285 Port Royal Road, Springfield, Virginia 22161.

TABLE OF CONTENTS

		Page
Chapter 1.	INTRODUCTION.	1
Chapter 2.	SUMMARY OF CHANGES SINCE PROPOSAL	2
Chapter 3.	SUMMARY OF PUBLIC COMMENTS AND RESPONSES. .	5
	Table 1. LIST OF COMMENTERS.	19

CHAPTER 1

INTRODUCTION

On November 18, 1980, the U. S. Environmental Protection Agency published in the Federal Register (45 FR 76346) revised Methods 106 and 107, "Determination of Vinyl Chloride from Stationary Sources," and "Determination of Vinyl Chloride Content of Inprocess Wastewater Samples, and Vinyl Chloride Content of Polyvinyl Chloride Resin, Slurry, Wet Cake, and Latex Samples," respectively. These revised methods were proposed under the authority of Sections 112, 114, and 301(a) of the Clean Air Act as amended.

Public comments were solicited at the time of proposal. The public comment period was from November 18, 1980, to January 19, 1981, and was extended to February 19, 1981.

Five comment letters were received concerning issues relative to the proposed test methods. A detailed discussion of these comments and responses are summarized in this document. The summary of comments and responses serves as the basis for the revisions which have been made to the test methods between proposal and promulgation..

CHAPTER 2

SUMMARY OF CHANGES SINCE PROPOSAL

1. Section 4.1, Method 106. Section 4.1.11 was added to list tubing fittings and connectors.

2. Section 5.2.3.2(b), Method 106 and Section 7.2.1.2(b), Method 107. The optional requirement of "...having it analyzed by the National Bureau of Standards," was changed to "...calibrating it against vinyl chloride cylinder standard reference materials (SRM's) prepared by the National Bureau of Standards, if such SRM's are available."

3. Section 5.2.4, Method 106. The last sentence of this section was deleted, and the following sentences were added: "Audit cylinders obtained from a commercial gas manufacturer may be used provided: (a) the gas manufacturer certifies the audit cylinders as described in Section 5.2.3.1 and (b) the gas manufacturer obtains an independent analysis of the audit cylinders to verify his analysis. Independent analysis is defined here to mean analysis performed by an individual different than the individual who performs the gas manufacturer's analysis, while using calibration standards and analysis equipment different from those used for the gas manufacturer's analysis. Verification is complete and acceptable when the independent analysis concentration is within ± 5 percent of the gas manufacturer's concentration."

4. Section 6.1, Method 106. The second sentence was revised to read, "A bag leak check should have been performed previously according to Section 7.3.2." The fifth sentence was revised to read, "After

allowing sufficient time to purge the line several times, change the vacuum line from the container to the bag and evacuate the bag until the rotameter indicates no flow."

5. Section 6.4, Method 106. The sixth sentence was revised to read, "Purge the sample loop for 30 seconds at the rate of 100 ml/min, shut off flow, allow the sample loop pressure to reach atmospheric pressure as indicated by the H_2O manometer, then activate the sample valve."

6. Section 7.1, Method 106. Reference to Figure 106-2 was deleted, and Figure 106-2 was deleted.

7. Section 7.2.2, Method 106. The last sentence was revised to read, "Perform calibration daily, or before and after the analysis of each emission test set of bag samples, whichever is more frequent." Two sentences were added that read, "For each group of sample analyses, use the average of the two calibration curves which bracket that group to determine the respective sample concentrations. If the two calibration curves differ by more than 5 percent from their mean value, then report the final results by both calibration curves."

8. Section 8.2, Method 106. The second sentence was revised to read, "From the calibration curves described in Section 7.2.2, determine the average concentration value of vinyl chloride, C_c, that corresponds to A_c, the sample peak area."

9. Section 6.2, Method 107. In Section 6.2.1, the part numbers were revised to indicate the new, correct numbers.

10. Section 6.2, Method 107. Section 6.2.4 was added to list a 100 µl syringe (optional).

11. Section 8.2.1, Method 107. The fifth sentence was revised to read, "Obtain the exact sample weight, add 100 µl or about two equal drops of distilled water, and immediately seal the vial."

12. Section 8.2.4, Method 107. The last sentence was revised to read, "Prepressurize the vial, and then condition for 1 to 2 hours as required at 90° C in the analyzer bath."

13. Section 8.3.1.1, Method 107. A sentence was added to indicate that a clean burr-free needle is mandatory.

14. Section 8.3.1.2(b), Method 107. The dosing line temperature was changed from 170° C to 150° C.

15. Section 8.3.2, Method 107. Quotation marks were added to the term "analysis time."

16. Section 9.1, Method 107. Wording was added to optionally allow the addition of 100 µl of distilled water in place of two drops.

CHAPTER 3

SUMMARIES OF PUBLIC COMMENTS AND RESPONSES

1. IV-D-1

Summary of Comment: The Agency (EPA) should publish a notice in the Federal Register to clarify the November 18, 1980 notice on Test Methods 106 and 107 as to whether the changes in the methods are proposed or final amendments.

Response to Comment: A notice was published in the Federal Register on January 6, 1981, Volume 46, No. 3, p. 1318, to clarify that the changes in Methods 106 and 107 published on November 18, 1980, were proposed changes.

2. IV-D-2

Summary of Comment: Commenter IV-D-2 requests that Section 5.2.4 of Test Method 106, entitled "Audit Cylinder Standards" further describe commercial gas manufacturers as an alternative source of these standards. Section 5.2.4 of Method 106 as proposed November 18, 1980, contains the following statements:

> "When available, the tester may obtain audit cylinders by contacting: Environmental Protection Agency, Environmental Monitoring Systems Laboratory, Quality Assurance Division (MD-77), Research Triangle Park, North Carolina 27711. If Audit cylinders are not available at the Environmental Protection Agency, the tester must secure an alternative source."

Response to Comment: The last sentence of Section 5.2.4 will be deleted and several sentences will be added to describe the acceptability of audit cylinders obtained from commercial gas manufacturers.

3. IV-D-3

Summary of Comment: Section 7.2.2 of Test Method 106 should be changed to require calibration at least once every 8 hours of continuous operation of the gas chromatograph, whereas the method presently requires daily calibration. If this change would require too much time to analyze all standards, then at least two of the standard mixtures could be analyzed every 8 hours. Then the values generated could be compared to the last complete calibration curve. If the new values deviate more than 5 percent from the curve, then a new calibration curve would have to be prepared.

Response to Comment: Section 7.2.2 requires that calibration be performed daily, or before and after each set of bag samples, whichever is more frequent. While analysis of a set of Method 106 samples rarely takes more than 8 hours, it would be an unnecessary burden to arbitrarily set 8 hours as a cutoff point for valid calibrations. A sentence will be added, however, to indicate that if calibration curves deviate by more than 5 percent from their mean, then the results must be reported by both calibration curves.

4. IV-D-4

Summary of Comment: For Method 106, a leak between the bag inlet and probe can have a significant effect on the sample. Therefore, there should be a requirement for leak checking this portion of the sample system.

Response to Comment: There are no significant pressure drops when sample is flowing through this portion of the sample train;

therefore, the requirement to check that all connectors between the bag and probe are tight should be sufficient.

5. IV-D-4

Summary of Comment: Add a Section 4.1.11 to Method 106 as follows: "4.1.11, Fittings and Connectors. All fittings (compression type or otherwise) used in connecting the sample line from the probe to the box should be Teflon or stainless steel. Tygon or surgical rubber tubing may be used to hold two pieces of Teflon tubing together, provided one tubing end is flush against the other or fits inside the other."

Response to Comment: This suggested addition may be helpful to some, and will therefore be added. However, slip connections will not be suggested as they are prone to leakage.

6. IV-D-4

Summary of Comment: Section 4.3.1 of Method 106 should be revised to include a combination plotter/integrator, thereby precluding the problem of sources having to ask if they can be used.

Response to Comment: Section 4.3.8 already describes a strip chart recorder as optionally equipped with either a disc or electronic integrator, so no further description should be necessary.

7. IV-D-4

Summary of Comment: In reference to Section 4.3.1, heating the sample loop should not be mandatory because not all labs will have a heated valve. It should be sufficient to insulate the valve/loop and insert a thermometer tip underneath the insulation so that the temperature is known.

Response to Comment: A heated sample loop is necessary to prevent sample intercontamination. A sample valve can be heated by using a heat tape and rheostat, both of which are readily obtainable.

8. IV-D-4

Summary of Comment: Section 4.3.4 of Method 106 should be revised to indicate that the regulators used be ones specified by the gas manufacturer, because it is especially important that proper regulators be used on calibration gas cylinders.

Response to Comment: No contamination problems resulting from the interchange of regulators can be foreseen. If only the regulators specified by the gas manufacturer are required, then unnecessary expenses may be incurred.

9. IV-D-4

Summary of Comment: Add a Section 4.4.5 to Method 106 as follows:

"4.4.5. Midget Impinger. For use in preparation of vinyl chloride standards; made of Pyrex glass, with a minimum of grease applied to the ground glass joint."

Response to Comment: The midget impinger is not required, as Figure 106-2 is in error. Refer to the response to the comment about Section 7.1 (See No. 13).

10. IV-D-4

Summary of Comment: Section 6.1 of Method 106 should be revised to read as follows (changes are underlined):

"Assemble the sample train as shown in Figure 106-1. <u>The bag and rigid container should have been leak-checked</u> (7.3.2) <u>prior to</u>

setting up for sample collection. Using a suitable coupler, connect the vacuum line to the sample line. Place the end of the probe at the centroid of the stack, and start the pump with the needle valve adjusted to yield a flow that will fill over 50 percent of the bag volume in the specified sample period. After allowing sufficient purge time to displace the sample line volume several times, disconnect the vacuum and sample lines; then connect the vacuum line to the bag, and evacuate the bag until the rotameter indicates no flow. (If the bag has been leak-checked and flow is still indicated, there may be a leak in the bag-to-quick-connect connection. This should be fixed before proceeding further.) Start the sample by connecting the sample line to the bag and the vacuum line to the container, as illustrated in Figure 106-1. During the sampling period, keep a constant proportionality between the sample flow rate and stack flow rate. At all times . . . ."

Response to Comment: The procedure is essentially correct as proposed. The intent is to prefill the sample bag with some sample, and then reevacuate the bag while simultaneously making another leak check. The proposed wording of this section will be slightly changed to clarify this intent.

11. IV-D-4

Summary of Comment: Section 6.3 of Method 106 needs refinement. If a pump is used, it should be placed upstream of the rotameter and downstream of the pressure gauge. Obviously, some vacuum will be

created in the line. In the case of micro sampling valves (Carle or Valco) with 1/16-inch tubing connections, the vacuum may be too high for measurement with a 1-inch water manometer. In using the option of container pressurization, flow control should be by means of a needle valve upstream of the sample valve. Otherwise, there is a possibility of pressurizing the sample loop. Having the water manometer downstream of the charcoal filter may not result in an accurate measurement of the absolute sample loop pressure.

Response to Comment: The object of the 1-inch H_2O pressure gauge (not manometer) is to determine that gas in the sample loop has returned to atmospheric pressure, after sample flow has been stopped. Container pressurization to move sample gas through the sample loop should not harm the sample loop.

12. IV-D-4

Summary of Comment: In Section 6.4 of Method 106 as proposed, the sixth sentence apparently has a phrase missing. It should read "Purge the sample loop for 30 seconds at the rate of 100 ml/min, shut off flow, allow the pressure to drop to atmospheric, as indicated by manometer zero, then activate the sample valve."

Response to Comment: While Section 6.3 already describes this operation, it may clarify the procedure to repeat it in Section 6.4, so Section 6.4 will be revised to include this suggestion.

13. IV-D-4

Summary of Comment: Section 7.1 of Method 106, as proposed, makes reference to Figure 106-2. However, instructions say to inject vinyl

chloride through the wall of the bag. Figure 106-2 indicates that the vinyl chloride is to be injected through a septum on the top of the midget impinger.

Response to Comment: Figure 106-2 illustrates a standards preparation procedure not described in the optional standard preparation section, and therefore Figure 106-2 will be dropped. It is also felt that the actual standards preparation procedure would not be enhanced by a figure, so none will be added.

14. IV-D-5

Summary of Comment: The commenter had previously requested and received approval of an alternative procedure to Test Method 107. The commenter (IV-D-5) is concerned as to whether or not the promulgation of a modified Method 107 will mean that approval of his alternative procedure will be recinded.

Response to Comment: The proposed changes in EPA Method 107 are meant to enhance the performance of that method, and should not be interpreted as having any bearing on the prior approval of alternative test methods.

15. IV-D-5

Summary of Comment: In reference to Section 6.2.1 of Method 107 as proposed, Perkin-Elmer Part No. 105-0118 is no longer a valid part number for vials, seals, and caps. The correct part numbers are as follows:

Vials: 0105-0129, Septa: 8001-0728 (gray butyl rubber septum, plug style) and 0105-0131 (butyl rubber septa).

Response to Comment: The commenter is correct, and the revised part numbers will be included.

16. IV-D-5

Summary of Comment: The proposed procedure of Section 6.3.2 of Method 107 suggests the use of Porapak Q columns. The commenter has not been able to get separation of vinyl chloride and acetaldehyde with the Porapak Q column. The commenter uses two 1.83 meter columns containing 1 percent Supelco 1000 on Carbopak B, which give adequate separation of vinyl chloride and acetaldehyde.

Response to Comment: Section 6.3.2 of Method 107, as proposed, already lists columns for the separation of vinyl chloride and acetaldehyde. Other columns can also be acceptable, as described in Section 6.3.2.

17. IV-D-5

Summary of Comment: Section 6.3.10 of Method 107, as proposed, deals with a proposed addition to this procedure, the head space vial prepressurizer. The commenter's analysts indicate that the prepressurization step was introduced because the authors of Method 107 felt that pressurization just prior to injection, as in the old procedure, did not allow adequate time for the vapors and the head space to reach equilibrium. A spot comparison by the commenter shows no significant difference between the old procedure and the new prepressurization procedure. In addition, the commenter has had several problems with leakage once the vials have been prepressurized. They have found that when butyl rubber septa are used, leaks appear

through the hole in the septum made by the prepressurization apparatus after the vial has been pressurized; in addition, when Teflon-faced septa are used as specified in sampling waste water, they have experienced great difficulty in sealing the vials so as to preclude leaks around the sides of the septa. They have found, however, that the use of butyl rubber septa is more appropriate in the sampling of waste water, both from the standpoint of expense and sealability. These comments on the prepressurization also apply to paragraphs 8.2, 8.2.3, and 8.2.4 of the proposed Method 107.

Response to Comment: A reference will be added to Section 11, Bibliography, that explains the need for vial prepressurization. The Environmental Protection Agency agrees that Teflon septa should not be used on sample analysis vials. Rather, butyl rubber septa must be used as specified. Leaks can be greatly reduced by using a clean, burr-free injection needle, and a statement will be added to that effect.

18. IV-D-5

Summary of Comment: Section 8.2.1 of the proposed Method 107 requires the two drops of distilled water be added to the contents of the vial, i.e., resin samples, prior to sealing. The old procedure required that 100 microliters of distilled water must be injected into the vial after sealing and weighing using a 100 microliter syringe. Although it is just as easy to add two drops of water as it is to inject 100 microliters of water, most facilities are adapted to the old procedure and such a change could cause confusion in day-to-day laboratory operations.

Response to Comment: Calculations by EPA show that either 100 µl or two drops of water will saturate the sample analysis vial, so the method will be changed to indicate that either amount is satisfactory.

19. IV-D-5

Summary of Comment: Section 8.2.2 of Method 107, as proposed, specifies a dewatering procedure which is different from that in the old procedure. The commenter's alternative method is based upon the idea that an accurate weight of the dewatered resin be obtained, and further that the sample must be weighed to a specified weight to provide for ease in calculation. In this respect, the resulting wet cake, when dewatered by the proposed procedure, is much wetter than that in the old procedure, which makes accurate weighing to a specified weight virtually impossible. Therefore, it is suggested that the old dewatering procedure, i.e., that which is employed in existing Method 107, be retained in favor of the proposed dewatering procedure.

Response to Comment: The dewatering procedure was changed due to a concern that in vacuum filtering a sample, vinyl chloride might be removed from the sample wet cake. The Agency does not, however, have reason to disallow the old procedure as long as some control is exercised to keep the vacuum filtering of each sample to a minimum. Since in the revised procedure, all samples are weighed after placing in the sample analysis vial, no difficulty should be experienced with the requirement to weigh to a constant weight.

20. IV-D-5

Summary of Comment: Section 8.2.4 of the proposed Method 107 specifies a 2-hour conditioning time. Comparisons the commenter has made show that a 1-hour conditioning time gives the same result as a 2-hour conditioning time. Therefore, it is suggested that the procedure for a 1-hour conditioning time be retained.

Response to Comment: The change to 2-hours for sample conditioning was made as a result of a revised industry procedure. However, as 1 hour may be sufficient, EPA will change the procedure to allow a shorter conditioning time.

21. IV-D-5

Summary of Comment: Section 8.3.1.2 of the proposed Method 107 specifies a 170° C temperature for the dosing line. However, the F42 and F45 model chromatographs, do not provide for a temperature setting of 170°. These models only provide for selection of temperatures of 50, 100, 150, 200, and 250°. Table 1 shows a comparison of temperatures specified by the proposed procedure, by the old procedure, and the temperatures that the commenter uses both with an F42 and an F45 unit.

TABLE 1

Analysis (Temperature)

	Revised	Old	Commenter's Temperatures	
			F42	F45
Oven	140° C	50° C	105	105
Dosing Line	170° C	140° C	150	150
Injection block	170° C	140° C	170	170

The commenter believes that a temperature setting of 150° C should be specified for the dosing line.

Response to Comment: The commenter is correct as to the available temperature settings, so a change will be made to specify a temperature of 150° C for the dosing line.

22. IV-D-5

Summary of Comment: Section 8.3.2.b of the proposed Method 107 states, in programming the chromatograph analysis time, that "the normal setting is approximately 70 percent of the VCM retention time." This is a misstatement. The correct statement should be "VCM retention time is normally 70 percent of the analysis time." Table 2 sets forth the typical values the commenter has obtained using the F42 and F45 models.

Response to Comment: The commenter is correct in that the term "analysis time" as used in Section 8.3.2.b is a misnomer. The term is used to signal when backflushing is to occur, and the specified setting is correct. Quotation marks will be placed around the term to alleviate any further confusion.

TABLE 2

Retention and Analysis Time

	F42	F45
V.C. retention	2.2	2.4
Analysis time	3.4	3.8
Analysis time (V.C. RT/.70)	3.1	3.4

23. IV-D-5

Summary of Comment: In reference to Section 9.1 of the proposed Method 107, the commenter questions adding two drops of water prior to sealing the vial as opposed to injection of 100 microliters of water after sealing. Table 3 provided by the commenter shows responses for two trials on a 52 ppm VC standard comparing the addition of two drops of water vs. the injection of 100 microliters of water. These results show both a reduced and a more variable response when two drops of water are added as opposed to injection of 100 microliters. Therefore, the commenter suggests that in this paragraph, in addition to Section 8.2.1, that the method specify the injection of 100 microliters of distilled water after sealing of the vial.

TABLE 3. INTEGRATOR RESPONSE FOR 52 PPM VC STD

Trial 1		Trial 2	
2 Drops water	Injection 100 µl	2 Drops water	Injection 100 µl
13100	14724	12648	13621
14049	14595	11997	13874
13578	14353		14216
Avg. 13576	14558	Avg. 12322	14558
SD 474	190	SD 460	299

Response to Comment: A change will be made to allow either 100 µl or 2 drops of water. Refer to the response to the comment about Section 8.2.1.

24. IV-D-5

Summary of Comment: In reference to Section 9.2 of the proposed Method 107, the commenter feels that the proposed requirement that a straight line be drawn through the calibration points as derived by the Least Squares Method is an improvement over the old procedure.

Response to Comment: No response is required.

25. IV-D-5

Summary of Comment: In reference to Section 10.1 of the proposed Method 107, the commenter feels that the use of the calibration curve as proposed is an improvement over the old procedure.

Response to Comment: No response is required.

TABLE 1. LIST OF COMMENTERS

Docket No. A-80-50

Docket item No.	Commenter/Affiliation
IV-D-1	Scott W. Bowen, Associate, Beveridge, Fairbanks and Diamond 1333 New Hampshire Avenue, N.W. Washington, D.C. 20036
IV-D-2	Robert E. Squires, Operations Manager Scott Specialty Gases Division Scott Environmental Technology, Inc. Plumsteadville, Pa. 18949
IV-D-3	G. Vinson Hellwig, Senior Environmental Engineer PEDCo Environmental, Inc. Suite 503 505 South Duke Street Durham, N.C. 27701
IV-D-4	Robert E. James, Ph.D., Senior Scientist Engineering-Science 3109 North Interregional Austin, Texas 78722
IV-D-5	Thomas V. Malorzo, Senior Regulations Analyst 717 North Harwood Street Dallas, Texas 75201